

A PROCESS FOR THE HYDROPROCESSING OF HEAVY  
HYDROCARBON FEEDS USING AT LEAST TWO REACTORS

CROSS REFERENCE TO RELATED APPLICATIONS

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This application is based on PCT Application No. PCT/EP03/06033, filed on June 5, 2003, and claims priority from Japanese Patent Application No. 2002-169868, filed June 11, 2002, the content of both of said applications incorporated herein in their entirety.

10

BACKGROUND OF THE INVENTION

1. Field of the Invention

15 The present invention relates to a process for hydroprocessing a heavy hydrocarbon feed using hydroprocessing catalysts. More in particular, it relates to a hydroprocessing process for efficiently decreasing the sulfur, metals, nitrogen, and Conradson carbon residue (CCR) in a heavy hydrocarbon feed.

2. Prior Art

20 The heavy hydrocarbon oils such as atmospheric residues and vacuum residues that are produced when crude oils are refined contain large amounts of various impurities such as sulfur, metals, nitrogen, and Conradson carbon residue. In recent years there has been increasing use of these heavy hydrocarbon oils as feedstocks in hydroprocessing operations to remove  
25 impurities such as sulfur, so as to obtain a product suitable for use as fuel oils and also for conversion into more economically valuable light oils.

The impurities in the feedstock to be removed in the hydroprocessing operation include sulfur, Conradson carbon residue (CCR), various metals, more  
30 in particular nickel and vanadium, nitrogen and asphaltenes. The exact amounts of the various impurities to be removed differ from feedstock to feedstock.

Various processes for the hydroprocessing of heavy hydrocarbon feeds have been described in the art.

US 4,054,508 describes a three-zone process for the demetallization and hydrodesulfurization of hydrocarbon oils, preferably residual fractions, which can contain substantial amounts of asphaltenes. The first reaction zone contains a large-pore catalyst comprising a Group VIB metal, preferably Mo, on an alumina support, and having at least 60% of its pore volume in pores with a diameter of 100-200 Å, at least about 5% of its pore volume in pores with a diameter greater than 500 Å, and preferably a surface area of up to 110 m<sup>2</sup>/g. The second reaction zone contains a small-pore catalyst containing a hydrogenating component and having at least 50%, preferably at least 60%, of its pore volume in pores with a diameter of 30-100 Å, and a surface area of at least 150 m<sup>2</sup>/g. The third reaction zone contains the same catalyst as the first reaction zone but in a smaller amount. The large-pore catalyst has higher demetallization activity and lower hydrodesulfurization activity compared to the small-pore catalyst.

US 4,431,525 discloses a hydrotreating process of heavy hydrocarbon feedstocks containing asphaltenes, metals, nitrogen compounds, and sulfur compounds over a sequence of three catalysts. The first catalyst is a demetallization catalyst and has an average pore diameter of 12.5-35 nm, the second catalyst is a hydrodesulfurization catalyst and has an average pore diameter of 8-13 nm. The third catalyst, for which no purpose is given, contains Mo, Cr, and Co, and has a pore volume of 0.4-0.8 ml/g, a surface area of 150-300 m<sup>2</sup>/g, and an average pore diameter of 10-20 nm.

US 5,744,025 discloses a process for hydrotreating a metal-containing heavy hydrocarbon feedstock over a sequence of three catalysts. The first catalyst is a demetallization catalyst and has at least 40% of its pore volume in pores with a diameter of 17-25 nm and a surface area of 100-160 m<sup>2</sup>/g. The second catalyst, which can have demetallization and/or hydrodesulfurization

and/or hydrodenitrogenation and/or Conradson carbon residue removal activity, has at least 40% of its pore volume in pores with a diameter of 3-17 nm and a surface area of 160-350 m<sup>2</sup>/g. The third catalyst is stated to be a hydrodemetallization catalyst and comprises a Group VIB and a Group VIII  
5 hydrogenation metal component, preferably on alumina, and has at least 40%, preferably at least 60%, of its pore volume in pores with a diameter of 17-25 nm and a surface area of 100-160 m<sup>2</sup>/g.

Japanese laid-open patent application No. 2001-003066 discloses a  
10 process for hydrotreating heavy gas oils over a sequence of three catalysts with different pore size distributions, followed by a hydrodesulfurization reactor.

Japanese laid-open patent application No. 2000-351978 describes a process for the hydroprocessing of heavy hydrocarbon feeds wherein the feed is  
15 subjected to the sequential steps of hydrodemetallization, hydrodesulfurization, and the combination of isomerization and hydrodesulfurization.

#### SUMMARY OF THE INVENTION

In one embodiment, the present invention is a process for  
20 hydroprocessing a hydrocarbon feed containing Conradson carbon using at least two reactors in which the hydrocarbon feed is subjected sequentially to the steps of

- hydroprocessing in a first hydroprocessing reactor, in which it is subjected sequentially to a hydrodemetallisation step, a hydro-  
25 desulfurisation step carried out at a temperature higher than that of said hydrodemetallisation step, and an asphaltene removal step carried out at a temperature higher than that of said hydrodesulfurisation step,
- hydroprocessing in a second hydroprocessing reactor, in which it is  
30 subjected sequentially to a hydrodesulfurisation step and an

asphaltene removal step, which latter is carried out at a temperature higher than that of said hydrodesulfurisation step.

Other embodiments of the invention relate to details concerning catalyst  
5 composition and physical properties, process flow details and feed composition, all of which are described hereinbelow.

#### DETAILED DESCRIPTION OF THE INVENTION

A problem encountered in heavy feed hydroprocessing operations in  
10 which the removal of Conradson carbon residue is an important goal is the formation of sludge. The mechanism of sludge formation is believed to be as follows. Conradson carbon residue is considered to contain asphaltenes as its main component. Asphaltenes are complicated high-molecular materials made up of nuclei of condensed polycyclic aromatic hydrocarbons with saturated  
15 hydrocarbon chains and naphthenic rings bound to them. They also contain sulfur, nitrogen, and oxygen. They are insoluble in n-hexane and soluble in carbon disulfide and benzene. In the feedstock, asphaltenes are present in a dispersed form due to the presence of solvent components. However, if during the hydroprocessing operation the asphaltenes and the solvent components are  
20 hydrogenated to a too great extent, the asphaltenes cohere to form sludge (insoluble granular materials) and sediment.

If sludge is formed during a hydroprocessing operation, it settles and is deposited in the various parts of the refinery such as heat exchangers, reactors,  
25 etc. In so doing it can seriously disturb the hydroprocessing operation, even to the extent that the operation may have to be stopped prematurely.

Furthermore, the presence of sludge will lead to catalyst deactivation due to coke formation. As a result thereof, the operating temperature of the process  
30 needs to be increased to obtain the same product properties. This leads not only to a shortened cycle length, but also to a waste of energy.

Although the processes described in the above references work well in effecting hydrodemetallization and hydrosulfurization, there is still room for improvement. More in particular, there is need for a hydroprocessing process that can achieve efficient contaminant removal (hydrodemetallization, 5 hydrosulfurization, hydrodenitrogenation, Conradson carbon residue removal), wherein the removal of Conradson carbon residue and other contaminants is not accompanied by excessive sludge formation. The present invention solves this problem by providing the process described above.

10 The crux of the process according to the invention is that the feed is treated in two hydroprocessing reactors, with an asphaltene removal catalyst being present at the high-temperature end of both of the reactors. It is this particular feature of the present invention, which in combination with the specific reaction sequence, ensures that sludge formation is kept limited while efficient 15 contaminant removal is obtained. This combination of features makes for an efficient and highly stable process.

The entire effluent can be led from the first reactor to the second reactor, but it is also possible to lead only the liquid fraction from the first reactor to the 20 second reactor, or to lead only part of the liquid fraction from the first reactor to the second. It is preferred to lead the entire effluent or the entire liquid effluent to the further reactor. In the latter case, a gas/liquid stripper will be present between the reactors.

25 The option wherein the entire liquid effluent is led to the further reactor is considered most preferred at this point in time. The above also holds for streams from the second to any further reactor(s). It is possible to apply intermediate reactors between the two reactors having an asphaltene removal catalyst at the high-temperature end of both of the reactors. In that case, the 30 above also holds for streams to any intermediate reactor.

The feed can be led through the reactors from top to bottom or from bottom to top. Operation from top to bottom is most common. The catalyst sequences in the present application are given in the direction of the feed.

5        The reactors used in the process according to the invention are the ones conventionally used in hydroprocessing and oil refining. These reactors are generally adiabatic. It is preferred that the reactor is provided with a means for supplying hydrogen through a quench line, etc. for controlling the inside reaction temperature. Stripping equipment for removing hydrogen sulfide, ammonia, etc.  
10      can be installed between the reactors.

The different steps of the process according to the invention are carried out at different temperatures, with the temperature of the hydrodesulfurization step in the first reactor being higher than that of the hydrodemetallization step,  
15      while the temperature of the asphaltene removal step in its turn is higher than the temperature in the hydrodesulfurization step. In the second reactor, the temperature of the asphaltene removal step is higher again than the temperature in the hydrodesulfurization step in the second reactor.

20        The hydrodemetallization step in the first reactor is preferably carried out at a temperature of 300-400°C, more preferably 350-380°C.

The subsequent hydrodesulfurization step is carried out at a temperature above that of the hydrodemetallization step. The hydrodesulfurization  
25      temperature preferably is 320 to 420°C, more preferably 360-410°C.

The asphaltene removal step in the first reactor is carried out at a temperature which is higher than that of the hydrodesulfurization step. It is preferably carried out at a temperature of 350-450°C, more preferably 370-  
30      420°C.

The preferred temperature ranges for the hydrodesulfurization and the asphaltene removal step carried out in the second reactor and optional further reactors are the same as those given above for the corresponding processes in the first reactor.

5

The reaction temperatures given above for the various reaction zones are the average feed temperatures over the entire reaction zone filled with a certain type of catalyst. The temperature in the hydrodesulfurization zone generally is at least 2°C above the reaction temperature in the preceding demetallizationhydrodemetallization zone, preferably at least 4°C. The reaction  
10 temperature in the asphaltene removal zone generally is at least 2°C above the reaction temperature in the preceding hydrodesulfurization zone, preferably at least 4°C. This applies to all reactors which contain the specified reaction zones in the specified order.

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Other than the reaction temperature, the hydroprocessing conditions are not especially limited. Conventional hydroprocessing conditions may be applied. These include a hydrogen partial pressure of generally 2 to 22 MPa, preferably 10-20 MPa, a hydrogen to feedstock ratio of generally 300-1500 NI/I, preferably  
20 600-1000 NI/I, and a liquid hourly space velocity (LHSV) of generally 0.1-10 h<sup>-1</sup>, preferably 0.2-2.0 h<sup>-1</sup>.

Figure 1 is a process chart of the process according to the invention. As is illustrated in this figure, a hydrocarbon feed is first fed to a reactor 1, and  
25 passes through a low-temperature zone 11 containing a hydrodemetallization catalyst, an intermediate-temperature zone 12 containing a hydrodesulfurization catalyst, and a high-temperature zone 13 containing an asphaltene removal catalyst. The effluent from the first reactor is led to a reactor 2, where it is passed through a lower-temperature zone 21 containing a hydrodesulfurization  
30 catalyst and a higher-temperature zone 22 comprising an asphaltene removal

catalyst, resulting in the formation of a product that is discharged from the bottom of the reactor 2.

Figure 2 shows a variation on the process of the invention wherein a third  
5 reactor is present downstream of the reactors 1 and 2 described above for  
Figure 1. In this embodiment the effluent from reactor 2 is led to a third reactor  
3, where it is passed through a lower-temperature zone 31 containing a  
hydrodesulfurization catalyst and a higher-temperature zone 32 comprising an  
asphaltene removal catalyst, resulting in the formation of a product that is  
10 discharged from the bottom of the reactor 3.

Figure 3 shows a variation on the process according to the invention,  
wherein a reactor 2 containing only a hydrodesulfurization catalyst is applied  
between a reactor 1 which comprises, from inlet to outlet, a low-temperature  
15 zone 11 containing a hydrodemetallization catalyst, an intermediate-temperature  
zone 12 containing a hydrodesulfurization catalyst, and a high-temperature zone  
13 containing an asphaltene removal catalyst, and a reactor 3, which contains,  
from inlet to outlet, a lower-temperature zone 31 containing a  
hydrodesulfurization catalyst and a higher-temperature zone 32 comprising an  
20 asphaltene removal catalyst, resulting in the formation of a product that is  
discharged from the bottom of the reactor 3.

Figure 4 shows a further variation of the process according to the  
invention, wherein a third reactor is present downstream of the reactors 1 and 2  
25 described above for Figure 1. In this embodiment the effluent from reactor 2 is  
led to a third reactor 3, where it is passed through a hydrodesulfurization  
catalyst, resulting in the formation of a product that is discharged from the  
bottom of the reactor 3.



In all these embodiments it is preferred that the entire effluent, or the entire liquid effluent if a stripper is present between the reactors, is led to the further reactor.

5           It is preferred for the volume ratio in the first reactor of the hydrodemetallization catalyst layer, the hydrodesulfurization catalyst layer, and the asphaltene removal catalyst layer to be 3-50:30-95:2-30, more preferably 5-45:35-95:2-25.

10           It is preferred for the volume ratio in the second reactor between the hydrodesulfurization catalyst layer and the asphaltene removal catalyst layer to be 60-97:3-40, more preferably 65-97:3-35.

          If so desired, a limited amount of scale removal catalyst may be present in  
15   the top of the second and optionally further reactors. Scale removal catalysts are known to the skilled person. If present, the scale removal catalyst will generally be applied in an amount of 1-3 wt.%.

          As indicated above, it is possible to apply a third or even further reactors  
20   downstream of the second reactor, the third or further reactors containing, from inlet to outlet, a hydrodesulfurization catalyst and an asphaltene removal catalyst. The preferred volume range between the hydrodesulfurization catalyst and the asphaltene removal catalyst in the third and further reactors is within the same ranges as indicated above for the second reactor.

25

          The process of the present invention is particularly suitable for the hydroprocessing of heavy hydrocarbon feeds. It is particularly suitable for hydroprocessing heavy feedstocks of which at least 40 wt.%, preferably at least 60 wt.%, boils above 538°C (1000°F) and which comprise at least 0.1 wt.%,  
30   preferably at least 1 wt.%, of sulfur and at least 5 wt.% of Conradson carbon. The sulfur content of the feedstock may be above 2 wt.%. Its Conradson carbon

content may be above 8 wt.%, preferably above 10 wt.%. The feedstock will contain contaminant metals, such as nickel and vanadium. Typically, these metals are present in an amount of at least 15 wtppm, calculated on the total of Ni and V, more particularly in an amount of at least 30 wtppm.

5

Suitable feedstocks include atmospheric residue, vacuum residue, residues blended with gas oils, vacuum gas oils, coker gas oils, crudes, shale oils, tar sand oils, solvent deasphalted oil, coal liquefied oil, etc. Typically they are atmospheric residue (AR), vacuum residue (VR), and mixtures thereof.

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The hydrodemetallization catalyst used in the process according to the invention generally comprises a Group VIB metal component, preferably molybdenum, on a porous oxidic carrier. The catalyst may or may not also contain a Group VIII metal component, preferably nickel and/or cobalt, for reasons of economics and performance more preferably nickel. The Group VIB metal component is generally present in an amount of 1.5-20 wt.%, calculated as trioxide, more preferably 4-16 wt.%. If a Group VIII metal component is present in the hydrodemetallization catalyst, it is generally present in an amount of 0.3-6 wt.%, preferably 1-5 wt.%.

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The hydrodemetallization catalyst is based on a porous oxidic carrier. Preferably, the carrier comprises at least 50 wt.% of alumina, the balance being made up of oxides of one or more of silicon, titanium, or zirconium. Preferably, the carrier contains at least 75 wt.% of alumina, more preferably at least 95 wt.%.

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The hydrodemetallization catalyst may contain limited amounts of other ingredients known in the art as suitable for use in hydrodemetallization catalysts, including phosphorus, boron, alkaline metal components, and alkaline earth metal components.

30

The demetallizationhydrodemetallization catalyst has a total pore volume which is generally between 0.2 and 1.4 ml/g, preferably 0.4-1.2 ml/g, more preferably 0.5-0.9 ml/g.

5        The hydrodemetallization catalyst has a surface area of 50-250 m<sup>2</sup>/g, preferably 80-200 m<sup>2</sup>/g, more preferably 100-180 m<sup>2</sup>/g. If the surface area of the catalyst is too low, the catalytic activity will be insufficient. If the surface area of the catalyst is too high, the average pore diameter of the catalyst may be too low. The average pore diameter of the catalyst is defined in the context of the  
10    present specification as the pore diameter at which half of the pore volume is present in pores with a diameter above this value while the other half of the pore volume is present in pores with a diameter below this value. The hydrodemetallization catalyst used in the process according to the invention generally has an average pore diameter of 10-35 nm, preferably 15-30 nm, more  
15    preferably 20-30 nm, still more preferably 24-30 nm.

It is preferred for the hydrodemetallization catalyst used in the process according to the invention to have less than 15%, more preferably less than 10%, of pore volume present in pores with a diameter below 100 Å.  
20

Hydrodemetallization catalysts suitable for use in the present invention are known in the art. They are, e.g., commercially available from Nippon Ketjen Co. Ltd under the designations KFR 10, KFR 20, KFR 22, and KG 5.

25        The hydrodesulfurization catalyst to be used in the process according to the invention generally comprises a Group VIB metal component, preferably molybdenum, and a Group VIII metal component, preferably nickel and/or cobalt, more preferably nickel, on a porous oxidic carrier. The Group VIB metal component is generally present in an amount of 9-30 wt.%, calculated as  
30    trioxide, more preferably 10-27 wt.%. The Group VIII metal component is generally present in an amount of 2-12 wt.%, preferably 2-8 wt.%.

The hydrodesulfurization catalyst is based on a porous oxidic carrier. Preferably, the carrier comprises at least 50 wt.% of alumina, the balance being made up of oxides of one or more of silicon, titanium, or zirconium. Preferably,  
5 the carrier contains at least 75 wt.% of alumina, more preferably at least 95 wt.%.

The hydrodesulfurization catalyst may contain limited amounts of other ingredients known in the art as suitable for use in hydrodesulfurization catalysts,  
10 including phosphorus, boron, alkaline metal components, and alkaline earth metal components.

The hydrodesulfurization catalyst has a total pore volume which is generally between 0.2 and 1.4 ml/g, preferably 0.4-1.2 ml/g, more preferably 0.5-  
15 0.9 ml/g. The hydrodesulfurization catalyst generally has a surface area of 50-400 m<sup>2</sup>/g, preferably 100-300 m<sup>2</sup>/g, more preferably 200-300 m<sup>2</sup>/g. If the surface area of the catalyst is too low, the catalytic activity will be insufficient. If the surface area of the catalyst is too high, the average pore diameter of the catalyst may be too low. The hydrodesulfurization catalyst used in the process according  
20 to the invention generally has an average pore diameter of 5-20 nm, preferably 7-15 nm, more preferably 7-12 nm.

Hydrodesulfurization catalysts suitable for use in the present invention are known in the art. They are, e.g., commercially available from Nippon Ketjen Co.  
25 Ltd under the designations KFR 70, KFR 72, and KFR 70B.

The hydrodesulfurization catalyst used in the first reactor, the hydrodesulfurization catalyst used in the second reactor and any hydrodesulfurization catalyst(s) used in any further reactor may be the same or  
30 different.

The asphaltene removal catalyst used in the process according to the invention generally comprises a Group VIB metal component, preferably molybdenum, and a Group VIII metal component, preferably nickel and/or cobalt, more preferably nickel, on a porous oxidic carrier. The Group VIB metal component is generally present in an amount of 2-20 wt.%, calculated as trioxide, more preferably 4-16 wt.%. If the Group VIB metal content is too low, the activity of the catalyst will be impaired. If the Group VIB metal content is too high, the activity will not be improved further.

The Group VIII metal component is generally present in an amount of 0.5-6 wt.%, preferably 1-5 wt.%. If the Group VIII metal content is too low, the activity of the catalyst will be impaired. If the Group VIII metal content is too high, the activity will not be improved further.

The asphaltene removal catalyst is based on a porous oxidic carrier. Preferably, the carrier comprises at least 50 wt.% of alumina, the balance being made up of oxides of one or more of silicon, titanium, or zirconium. Preferably, the carrier contains at least 75 wt.% of alumina, more preferably at least 95 wt.%. The asphaltene removal catalyst may contain limited amounts of other ingredients known in the art, including phosphorus, boron, alkaline metal components, and alkaline earth metal components.

The asphaltene removal catalyst has a total pore volume which generally is at least 0.4 ml/g, preferably at least 0.55 ml/g. The pore volume generally is at most 1.4 ml/g, preferably at most 1.2 ml/g, more preferably at most 0.9 ml/g. The asphaltene removal catalyst generally has a surface area of at least 50 m<sup>2</sup>/g and at most 200 m<sup>2</sup>/g, preferably 100-180 m<sup>2</sup>/g.

If the surface area of the catalyst is too low, the catalytic activity will be insufficient. If the surface area of the catalyst is too high, the average pore diameter of the catalyst may be too low. The asphaltene removal catalyst used

in the process according to the invention generally has an average pore diameter of 10-35 nm, preferably 15-30 nm, more preferably 18-28 nm.

5 If the average pore diameter is too low, the decomposition of asphaltenes will be insufficient and excessive hydrogenation may take place to increase sludge formation. If the average pore diameter is too high, the asphaltene decomposition rate may also decrease, with inherent sludge formation.

10 It is preferred for the asphaltene removal catalyst used in the process according to the invention to have less than 15%, more preferably less than 10%, of pore volume present in pores with a diameter below 100 Å.

The asphaltene removal catalyst generally has 0.3 ml/g or less of pore volume in pores with a diameter of 100 nm or larger, preferably 0.2 ml/g or less.  
15 If the amount of pore volume present in this range is too high, the balance between the decomposition of the asphaltenes and the resins which act as their solvent is lost, and sludge is liable to be formed. Moreover, if the amount of pore volume present in this range is too high, the mechanical strength of the catalyst will decrease.

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Asphaltene removal catalysts suitable for use in the present invention are known in the art. They are, e.g., commercially available from Nippon Ketjen Co. Ltd under the designations KFR 10, KFR 20, KFR 22, and KG 5.

25 The asphaltene removal catalyst used in the first reactor, the asphaltene removal catalyst used in the second reactor, and any asphaltene removal catalyst(s) used in any further reactor may be the same or different.

30 As can be seen from the above description, the asphaltene removal catalyst and the hydrodemetallization removal catalyst used in the process according to the invention are quite similar. This means that it is within the

scope of the present invention for the demetallizationhydrodemetallization catalyst and the asphaltene removal catalyst to be used in the process according to the invention to be the same.

5           The hydrodesulfurization catalyst used in the process according to the invention is always different from the hydrodemetallization catalyst and the asphaltene removal catalyst. More in particular, the hydrodesulfurization catalyst has a Group VIB metal content which is at least 2 wt.%, preferably at least 3 wt.%, higher than the Group VIB metal content of the hydrodemetallization catalyst and the Group VIB metal content of the asphaltene removal catalyst,  
10           calculated as trioxide.

          Additionally, the average pore diameter of the hydrodesulfurization catalyst is at least 1 nm, preferably at least 2 nm, more preferably at least 3 nm,  
15           below the average pore diameter of the demetallizationhydrodemetallization catalyst and the average pore diameter of the asphaltene removal catalyst.

          The catalyst particles may have the shapes and dimensions common to the art. Thus, the particles may be spherical, cylindrical, or polylobal and their  
20           diameter may range from 0.5 to 10 mm. Particles with a diameter of 0.5-3 mm, preferably 0.7-2 mm, for example 1.2-1.5 mm, and a length of 1.5-10 mm, for example 2.5-4.5 mm, are preferred. Because they lead to a reduced pressure drop in demetallizationhydrodemetallization operations, polylobal particles may be preferred.

25

          If so desired, a small amount of the catalyst used in the top layer of one or more of the reactors may have a different particle shape and size for the purpose of regularising the flow of the feedstock passing through the reactor.

          As is conventional in the art, the various types of catalysts can be present in a  
30           single bed in the unit, or in a number of beds one above the other containing the same type of catalyst.

The way in which the catalysts used in the process according to the invention are prepared is not critical. By way of example, a suitable preparation process is described below.

5

A typical production process for preparing a catalyst carrier comprising alumina is coprecipitation of sodium aluminate and aluminum sulfate. The resulting gel is dried, extruded, and calcined, to obtain an alumina-containing carrier. Optionally, other components such as silica may be added before, during, or after precipitation. By way of example, a process for preparing an alumina gel will be described below.

First, a tank containing tap water or warm water is charged with an alkali solution of sodium aluminate, aluminum hydroxide or sodium hydroxide, etc., and an acidic aluminum solution of aluminum sulfate or aluminum nitrate, etc. is added for mixing. The hydrogen ion concentration (pH) of the mixed solution changes with the progress of the reaction. It is preferable that when the addition of the acidic aluminum solution is complete, the pH is 7 to 9, and that during mixing the temperature is 60 to 75°C. The mixture is then kept at that temperature for in general 0.5-1.5 hours, preferably for 40-80 minutes.

In a following stage, the gel is separated from the solution, and any commercially used washing treatment, for example a washing treatment using tap water or hot water, is carried out to remove impurities, mainly salts, from the gel. Then, the gel is shaped into particles in a manner known in the art, e.g., by way of extrusion, beading or pelletizing.

Finally, the shaped particles are dried and calcined. The drying is generally carried out at a temperature between room temperature and up to 200°C, generally in the presence of air. The calcining is generally carried out at a temperature of 300 to 950°C, preferably 600 to 900°C, generally in the



presence of air, for a period of 30 minutes to six hours. If so desired, the calcination may be carried out in the presence of steam to influence the crystal growth in the oxide.

5           By the above production process, it is possible to obtain a carrier having properties which will give a catalyst with the surface area, pore volume, and pore size distribution characteristics specified above. The surface area, pore volume, and pore size distribution characteristics can be adjusted in a manner known to the skilled person, for example by the addition during the mixing or shaping  
10 stage of an acid, such as nitric acid, acetic acid or formic acid, or other compounds as moulding auxiliary, or by regulating the water content of the gel by adding or removing water.

          The Group VIB metal components and, where appropriate, Group VIII  
15 metal components or other components such as phosphorus, can be incorporated into the catalyst carrier in a conventional manner, e.g., by impregnation and/or by incorporation into the support material before it is shaped into particles. At this point in time it is considered preferred to first prepare the carrier and incorporate the catalytic materials into the carrier after it has been  
20 dried and calcined.

          The metal components can be incorporated into the catalyst composition in the form of suitable precursors, preferably by impregnating the catalyst with an acidic or basic impregnation solution comprising suitable metal precursors. For  
25 the Group VIB metals, ammonium heptamolybdate, ammonium dimolybdate, and ammonium tungstenate may be mentioned as suitable precursors. Other compounds, such as oxides, hydroxides, carbonates, nitrates, chlorides, and organic acid salts, may also be used.

30           For the Group VIII metals, suitable precursors include oxides, hydroxides, carbonates, nitrates, chlorides, and organic acid salts. Carbonates and nitrates

are particularly suitable. The impregnation solution, if applied, may contain other compounds the use of which is known in the art, such as organic acids, e.g., citric acid, ammonia water, hydrogen peroxide water, gluconic acid, tartaric acid, malic acid or EDTA (ethylenediamine tetraacetic acid).

5

It will be clear to the skilled person that there is a wide range of variations on this process. Thus, it is possible to apply a plurality of impregnating stages, the impregnating solutions to be used containing one or more of the component precursors that are to be deposited, or a portion thereof. Instead of impregnating techniques, dipping processes, spraying processes, etc. can be used. In the case of multiple impregnation, dipping, etc., drying and/or calcining may be carried out in between.

After the metals have been incorporated into the catalyst composition, it is optionally dried, e.g., in air flow for about 0.5 to 16 hours at a temperature between room temperature and 200°C, and subsequently calcined, generally in air, for about 1 to 6 hours, preferably 1-3 hours, at 200-800°C, preferably 450-700°C. The drying is done to physically remove the deposited water. The calcining is done to bring at least part, preferably all, of the metal component precursors to the oxide form.

It may be desirable to convert the catalysts, i.e., the Group VIB and optional Group VIII metal components present therein, into the sulfidic form prior to their use in the hydroprocessing of hydrocarbon feedstocks. This can be done in an otherwise conventional manner, e.g., by contacting the catalyst in the reactor at increasing temperature with hydrogen and a sulfur-containing feedstock, or with a mixture of hydrogen and hydrogen sulfide. *Ex situ* presulfiding is also possible.

In the present specification, the indications Group VIB metal and a Group VIII metal refer to the Periodic Table of Elements applied by Chemical Abstract

Services (CAS system). The specific surface area is determined by nitrogen ( $N_2$ ) adsorption using the BET method.

5        The determination of the total pore volume and the pore size distribution is effected via mercury penetration at a contact angle of  $140^\circ$  with a surface tension of 480 dynes/cm, using, for example, a mercury porosimeter Autopore II (trade name) produced by Micrometrics.

Examples:

10        Three catalysts were selected for use in the present example. The hydrodemetallization (HDM) catalyst contained 9 wt.% of molybdenum, calculated as oxide, and 2 wt.% of nickel, calculated as oxide, on an alumina carrier. The catalyst had an average pore diameter of 180 Å.

15        The hydrodesulfurization (HDS) catalyst contained 12 wt.% of molybdenum, calculated as oxide, and 3 wt.% of nickel, calculated as oxide, on an alumina carrier. The catalyst had an average pore diameter of 120 Å.

20        The asphaltene removal (HDA<sub>sp</sub>) catalyst contained 8.0 wt.% of molybdenum, calculated as oxide, and 2.2 wt.% of nickel, calculated as oxide, on an alumina carrier. The catalyst had an average pore diameter of 260 Å, a surface area of 130 m<sup>2</sup>/g, a total pore volume of 0.8 ml/g, and a pore volume in pores with a diameter of 1000 Å and larger of 0.25 ml/g.

25        The feedstock used in the present example was a South Sea atmospheric residue with the following properties:

Sulphur	0.2 wt. %
nitrogen	3 000 wt. ppm
Metals (nickel + vanadium)	70 wt. ppm
Conradson Carbon residue	7 wt. %
Asphaltenes <sup>1</sup>	2.5 wt. %
Density (15°C)	0.93 g/ml
Distillation properties ASTM-D 5307	
Initial boiling point	301°C
50 wt. %	563°C
70 wt. %	624°C

<sup>1</sup> matter insoluble in n-heptane

- A small reactor system consisting of three reactors connected in series
- 5 was packed with the selected catalysts. The packing of the reactors applied in Example 1 according to the invention and in the Comparative Example is given below:

	Example 1	Comparative Example
1 <sup>st</sup> reactor	HDM catalyst – 20 vol. % HDS catalyst – 55 vol. % HDAsp catalyst – 25 vol. %	HDM catalyst – 20 vol. % HDS catalyst – 80 vol. %
2 <sup>nd</sup> reactor	HDS catalyst – 75 vol. % HDAsp catalyst – 25 vol. %	HDS catalyst – 100 vol. %
3 <sup>rd</sup> reactor	HDS catalyst – 95 vol. % HDAsp catalyst – 5 vol. %	HDS catalyst – 100 vol. %

- 10 After packing the reactor system with the respective catalysts, the catalysts were sulfided in a conventional manner by contacting them with a light gas oil (LGO) containing 2.5 wt. % of dimethyl disulfide (DMDS), and the feedstock described above was led to the reactor system at a pressure of 16.5 MPa, a liquid hourly space velocity (LHSV) of 0.3 h<sup>-1</sup>, and a hydrogen to feed
- 15 ratio (H<sub>2</sub>/oil ratio) of 850 NI/l. The reaction temperature was adjusted to achieve

a Conradson Carbon residue content of 3.0 wt.% in the product oil, with the temperature in the second bed being higher than the temperature in the first bed in each reactor, while, if applicable, the temperature in the third bed was higher than the temperature in the second bed. The test was carried out for a period of  
5 200 days.

In Example 1, where an asphaltene removal catalyst was present in the high-temperature bottom region of each of the three reactors, the process still operated well after 200 days, and could be continued after that date. By  
10 comparison, the process of the Comparative Example, where no asphaltene removal catalyst was present in the high-temperature bottom region of each of the three reactors, had to be discontinued on day 135, because the reactors were clogged with sludge.

15 The following table gives the temperatures of the various catalyst layers in Example 1 and the comparative Example.

	Example 1 (day 200)		Comparative Example (day 135)	
1 <sup>st</sup> reactor	HDM catalyst	390°C	HDM catalyst	390°C
	HDS catalyst	398°C	HDS catalyst	400°C
	HDAsp catalyst	405°C		
2 <sup>nd</sup> reactor	HDS catalyst	413°C	HDS catalyst	413°C
	HDAsp catalyst	422°C		
3 <sup>rd</sup> reactor	HDS catalyst	421°C	HDS catalyst	422°C
	HDAsp catalyst	423°C		

The processes of Example 1 and the Comparative Example were  
20 operated under such a regimen that the amount of Conradson carbon residue in the product was kept at 3.0 wt.%. This means that, as is conventional in the art of hydroprocessing, the reaction temperature is slowly increased to compensate

for catalyst deactivation to keep the amount of Conradson Carbon residue in the product at the desired value.

Figure 4 shows the change of the average reaction temperature during the process at a constant Conradson Carbon content in the product for the process according to the invention and for the Comparative Example. It can be seen that for the process according to the invention of Example 1, the temperature increase stabilised to a value of less than 0.8°C per month. In contrast, for the Comparative Example, by the end of the run a temperature increase of 2°C per month was obtained.

Apparently, even if the Conradson Carbon Content of the product is the same, the presence of an asphaltene removal catalyst in the high-temperature bottom end of the hydroprocessing reactors ensures that less sludge is formed, which leads to less clogging of the unit and a longer and more stable operation. The presence of the asphaltene removal catalyst also appears to result in a more stable process, as can be seen from a lower increase in reaction temperature being necessary to keep the Conradson carbon content of the product at a value of 3.0 wt.%.

20

Although not wishing to be bound by theory, the inventors believe that the presence of an asphaltene removal catalyst in the high-temperature lower end of the hydroprocessing reactors ensures that the decomposition of the asphaltenes and the resins which act as their solvents is well balanced, resulting in low sludge formation. On the other hand, it is believed that in the comparative example, where no asphaltene removal catalyst was present, the resins that act as solvent for the asphaltenes were hydrogenated. As a result, the asphaltenes became insoluble in the hydrocarbon feed, causing the formation of sludge. In turn, the presence of sludge caused deactivation of the catalyst due to coke being formed thereon.

30

## ABSTRACT

- The invention pertains to a process for hydroprocessing a heavy hydrocarbon feed using at least two reactors in which a heavy hydrocarbon feed is subjected
- 5 sequentially to the steps of
- hydroprocessing in a first hydroprocessing reactor, in which it is subjected sequentially to a hydrodemetallization step, a hydrodesulfurization step carried out at a temperature higher than that of said hydrodemetallization step, and an asphaltene removal step carried out at a temperature higher
  - 10 than that of said hydrodesulfurization step,
  - hydroprocessing in a second hydroprocessing reactor, in which it is subjected sequentially to a hydrodesulfurization step and an asphaltene removal step, which latter is carried out at a temperature higher than that of said hydrodesulfurization step.

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A PROCESS FOR THE HYDROPROCESSING OF HEAVY HYDROCARBON  
FEEDS USING AT LEAST TWO REACTORS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is based on PCT Application No. PCT/EP03/06033, filed on June 5, 2003, and claims priority from Japanese Patent Application No. 2002-169868, filed June 11, 2002, the content of both of said applications incorporated herein in their entirety.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for hydroprocessing a heavy hydrocarbon feed using hydroprocessing catalysts. More in particular, it relates to a hydroprocessing process for efficiently decreasing the sulfur, metals, nitrogen, and Conradson carbon residue (CCR) in a heavy hydrocarbon feed.

2. Prior Art

The heavy hydrocarbon oils such as atmospheric residues and vacuum residues that are produced when crude oils are refined contain large amounts of various impurities such as sulfur, metals, nitrogen, and Conradson carbon residue. In recent years there has been increasing use of these heavy hydrocarbon oils as feedstocks in hydroprocessing operations to remove impurities such as sulfur, so as to obtain a product suitable for use as fuel oils and also for conversion into more economically valuable light oils.

The impurities in the feedstock to be removed in the hydroprocessing operation include sulfur, Conradson carbon residue (CCR), various metals,



more in particular nickel and vanadium, nitrogen and asphaltenes. The exact amounts of the various impurities to be removed differ from feedstock to feedstock.

5 Various processes for the hydroprocessing of heavy hydrocarbon feeds have been described in the art.

US 4,054,508 describes a three-zone process for the demetallization and hydrodesulfurization of hydrocarbon oils, preferably residual fractions, which

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10 can contain substantial amounts of asphaltenes. The first reaction zone contains a large-pore catalyst comprising a Group VIB metal, preferably Mo, on an alumina support, and having at least 60% of its pore volume in pores with a diameter of 100-200 Å, at least about 5% of its pore volume in pores with a diameter greater than 500 Å, and preferably a surface area of up to 110 m<sup>2</sup>/g.

15 The second reaction zone contains a small-pore catalyst containing a hydrogenating component and having at least 50%, preferably at least 60%, of its pore volume in pores with a diameter of 30-100 Å, and a surface area of at least 150 m<sup>2</sup>/g. The third reaction zone contains the same catalyst as the first reaction zone but in a smaller amount. The large-pore catalyst has higher  
20 demetallization activity and lower hydrodesulfurization activity compared to the small-pore catalyst.

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US 4,431,525 discloses a hydrotreating process of heavy hydrocarbon feedstocks containing asphaltenes, metals, nitrogen compounds, and sulfur  
25 compounds over a sequence of three catalysts. The first catalyst is a demetallization catalyst and has an average pore diameter of 12.5-35 nm, the second catalyst is a hydrodesulfurization catalyst and has an average pore diameter of 8-13 nm. The third catalyst, for which no purpose is given, contains Mo, Cr, and Co, and has a pore volume of 0.4-0.8 ml/g, a surface area of 150-  
30 300 m<sup>2</sup>/g, and an average pore diameter of 10-20 nm.

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US 5,744,025 discloses a process for hydrotreating a metal-containing heavy hydrocarbon feedstock over a sequence of three catalysts. The first catalyst is a demetallization catalyst and has at least 40% of its pore volume in pores with a diameter of 17-25 nm and a surface area of 100-160 m<sup>2</sup>/g. The second catalyst, which can have demetallization and/or hydrodesulfurization and/or hydrodenitrogenation and/or Conradson carbon residue removal activity, has at least 40% of its pore volume in pores with a diameter of 3-17 nm and a surface area of 160-350 m<sup>2</sup>/g. The third catalyst is stated to be a hydrodemetallization catalyst and comprises a Group VIB and a Group VIII hydrogenation metal component, preferably on alumina, and has at least 40%, preferably at least 60%, of its pore volume in pores with a diameter of 17-25 nm and a surface area of 100-160 m<sup>2</sup>/g.

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Japanese laid-open patent application No. 2001-003066 discloses a process for hydrotreating heavy gas oils over a sequence of three catalysts with different pore size distributions, followed by a hydrodesulfurization reactor.

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Japanese laid-open patent application No. 2000-351978 describes a process for the hydroprocessing of heavy hydrocarbon feeds wherein the feed is subjected to the sequential steps of hydrodemetallization, hydrodesulfurization, and the combination of isomerization and hydrodesulfurization.

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## SUMMARY OF THE INVENTION

In one embodiment, the present invention is a process for hydroprocessing a hydrocarbon feed containing Conradson carbon using at least two reactors in which the hydrocarbon feed is subjected sequentially to the steps of

- hydroprocessing in a first hydroprocessing reactor, in which it is subjected sequentially to a hydrodemetallisation step, a hydro-

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desulfurisation step carried out at a temperature higher than that of said hydrodemetallisation step, and an asphaltene removal step carried out at a temperature higher than that of said hydrodesulfurisation step.

- hydroprocessing in a second hydroprocessing reactor, in which it is subjected sequentially to a hydrodesulfurisation step and an asphaltene removal step, which latter is carried out at a temperature higher than that of said hydrodesulfurisation step.

Other embodiments of the invention relate to details concerning catalyst composition and physical properties, process flow details and feed composition, all of which are described hereinbelow.

#### DETAILED DESCRIPTION OF THE INVENTION

A problem encountered in heavy feed hydroprocessing operations in which the removal of Conradson carbon residue is an important goal is the formation of sludge. The mechanism of sludge formation is believed to be as follows. Conradson carbon residue is considered to contain asphaltenes as its main component. Asphaltenes are complicated high-molecular materials made up of nuclei of condensed polycyclic aromatic hydrocarbons with saturated hydrocarbon chains and naphthenic rings bound to them. They also contain sulfur, nitrogen, and oxygen. They are insoluble in n-hexane and soluble in carbon disulfide and benzene. In the feedstock, asphaltenes are present in a dispersed form due to the presence of solvent components. However, if during the hydroprocessing operation the asphaltenes and the solvent components are hydrogenated to a too great extent, the asphaltenes cohere to form sludge (insoluble granular materials) and sediment.

If sludge is formed during a hydroprocessing operation, it settles and is deposited in the various parts of the refinery such as heat exchangers, reactors,

etc. In so doing it can seriously disturb the hydroprocessing operation, even to the extent that the operation may have to be stopped prematurely.

Furthermore, the presence of sludge will lead to catalyst deactivation due to coke formation. As a result thereof, the operating temperature of the process needs to be increased to obtain the same product properties. This leads not only to a shortened cycle length, but also to a waste of energy.

Although the processes described in the above references work well in effecting hydrodemetallization and hydrodesulfurization, there is still room for improvement. More in particular, there is need for a hydroprocessing process that can achieve efficient contaminant removal (hydrodemetallization, hydrodesulfurization, hydrodenitrogenation, Conradson carbon residue removal), wherein the removal of Conradson carbon residue and other contaminants is not accompanied by excessive sludge formation.

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The present invention solves this problem by providing the process described above.

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**Deleted:** for hydroprocessing a heavy hydrocarbon feed using at least two reactors in which a heavy hydrocarbon feed is subjected sequentially to the steps of ¶ <#>hydroprocessing in a first hydroprocessing reactor, in which it is subjected sequentially to a hydrodemetallisation step, a hydrodesulfurisation step carried out at a temperature higher than that of said hydrodemetallisation step, and an asphaltene removal step carried out at a temperature higher than that of said hydrodesulfurisation step, ¶ hydroprocessing in a second hydroprocessing reactor, in which it is subjected sequentially to a hydrodesulfurisation step and an asphaltene removal step, which latter is carried out at a temperature higher than that of said hydrodesulfurisation step.

The crux of the process according to the invention is that the feed is treated in two hydroprocessing reactors, with an asphaltene removal catalyst being present at the high-temperature end of both of the reactors. It is this particular feature of the present invention, which in combination with the specific reaction sequence, ensures that sludge formation is kept limited while efficient contaminant removal is obtained. This combination of features makes for an efficient and highly stable process.

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The entire effluent can be led from the first reactor to the second reactor, but it is also possible to lead only the liquid fraction from the first reactor to the second reactor, or to lead only part of the liquid fraction from the first reactor to the second. It is preferred to lead the entire effluent or the entire liquid effluent

to the further reactor. In the latter case, a gas/liquid stripper will be present between the reactors.

The option wherein the entire liquid effluent is led to the further reactor is considered most preferred at this point in time. The above also holds for streams from the second to any further reactor(s). It is possible to apply intermediate reactors between the two reactors having an asphaltene removal catalyst at the high-temperature end of both of the reactors. In that case, the above also holds for streams to any intermediate reactor.

The feed can be led through the reactors from top to bottom or from bottom to top. Operation from top to bottom is most common. The catalyst sequences in the present application are given in the direction of the feed.

The reactors used in the process according to the invention are the ones conventionally used in hydroprocessing and oil refining. These reactors are generally adiabatic. It is preferred that the reactor is provided with a means for supplying hydrogen through a quench line, etc. for controlling the inside reaction temperature. Stripping equipment for removing hydrogen sulfide, ammonia, etc. can be installed between the reactors.

The different steps of the process according to the invention are carried out at different temperatures, with the temperature of the hydrodesulfurization step in the first reactor being higher than that of the hydrodemetallization step, while the temperature of the asphaltene removal step in its turn is higher than the temperature in the hydrodesulfurization step. In the second reactor, the temperature of the asphaltene removal step is higher again than the temperature in the hydrodesulfurization step in the second reactor.

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The hydrodemetallization step in the first reactor is preferably carried out at a temperature of 300-400°C, more preferably 350-380°C.

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The subsequent hydrodesulfurization step is carried out at a temperature above that of the hydrodemetallization step. The hydrodesulfurization temperature preferably is 320 to 420°C, more preferably 360-410°C.

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The asphaltene removal step in the first reactor is carried out at a temperature which is higher than that of the hydrodesulfurization step. It is preferably carried out at a temperature of 350-450°C, more preferably 370-420°C.

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The preferred temperature ranges for the hydrodesulfurization and the asphaltene removal step carried out in the second reactor and optional further reactors are the same as those given above for the corresponding processes in the first reactor.

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The reaction temperatures given above for the various reaction zones are the average feed temperatures over the entire reaction zone filled with a certain type of catalyst. The temperature in the hydrodesulfurization zone generally is at least 2°C above the reaction temperature in the preceding demetallizationhydrodemetallization zone, preferably at least 4°C. The reaction temperature in the asphaltene removal zone generally is at least 2°C above the reaction temperature in the preceding hydrodesulfurization zone, preferably at least 4°C. This applies to all reactors which contain the specified reaction zones in the specified order.

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Other than the reaction temperature, the hydroprocessing conditions are not especially limited. Conventional hydroprocessing conditions may be applied. These include a hydrogen partial pressure of generally 2 to 22 MPa, preferably 10-20 MPa, a hydrogen to feedstock ratio of generally 300-1500 NI/I, preferably 600-1000 NI/I, and a liquid hourly space velocity (LHSV) of generally 0.1-10 h<sup>-1</sup>, preferably 0.2-2.0 h<sup>-1</sup>.

Figure 1 is a process chart of the process according to the invention. As is illustrated in this figure, a hydrocarbon feed is first fed to a reactor 1, and passes through a low-temperature zone 11 containing a hydrodemetallization catalyst, an intermediate-temperature zone 12 containing a hydrodesulfurization catalyst, and a high-temperature zone 13 containing an asphaltene removal catalyst. The effluent from the first reactor is led to a reactor 2, where it is passed through a lower-temperature zone 21 containing a hydrodesulfurization catalyst and a higher-temperature zone 22 comprising an asphaltene removal catalyst, resulting in the formation of a product that is discharged from the bottom of the reactor 2.

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Figure 2 shows a variation on the process of the invention wherein a third reactor is present downstream of the reactors 1 and 2 described above for Figure 1. In this embodiment the effluent from reactor 2 is led to a third reactor 3, where it is passed through a lower-temperature zone 31 containing a hydrodesulfurization catalyst and a higher-temperature zone 32 comprising an asphaltene removal catalyst, resulting in the formation of a product that is discharged from the bottom of the reactor 3.

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Figure 3 shows a variation on the process according to the invention, wherein a reactor 2 containing only a hydrodesulfurization catalyst is applied between a reactor 1 which comprises, from inlet to outlet, a low-temperature zone 11 containing a hydrodemetallization catalyst, an intermediate-temperature zone 12 containing a hydrodesulfurization catalyst, and a high-temperature zone 13 containing an asphaltene removal catalyst, and a reactor 3, which contains, from inlet to outlet, a lower-temperature zone 31 containing a hydrodesulfurization catalyst and a higher-temperature zone 32 comprising an asphaltene removal catalyst, resulting in the formation of a product that is discharged from the bottom of the reactor 3.

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Figure 4 shows a further variation of the process according to the invention, wherein a third reactor is present downstream of the reactors 1 and 2 described above for Figure 1. In this embodiment the effluent from reactor 2 is led to a third reactor 3, where it is passed through a hydrodesulfurization catalyst, resulting in the formation of a product that is discharged from the bottom of the reactor 3.

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In all these embodiments it is preferred that the entire effluent, or the entire liquid effluent if a stripper is present between the reactors, is led to the further reactor.

It is preferred for the volume ratio in the first reactor of the hydrodemetallization catalyst layer, the hydrodesulfurization catalyst layer, and the asphaltene removal catalyst layer to be 3-50:30-95:2-30, more preferably 5-45:35-95:2-25.

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It is preferred for the volume ratio in the second reactor between the hydrodesulfurization catalyst layer and the asphaltene removal catalyst layer to be 60-97:3-40, more preferably 65-97:3-35.

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If so desired, a limited amount of scale removal catalyst may be present in the top of the second and optionally further reactors. Scale removal catalysts are known to the skilled person. If present, the scale removal catalyst will generally be applied in an amount of 1-3 wt.%.

As indicated above, it is possible to apply a third or even further reactors downstream of the second reactor, the third or further reactors containing, from inlet to outlet, a hydrodesulfurization catalyst and an asphaltene removal catalyst. The preferred volume range between the hydrodesulfurization catalyst and the asphaltene removal catalyst in the third and further reactors is within the same ranges as indicated above for the second reactor.

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The process of the present invention is particularly suitable for the hydroprocessing of heavy hydrocarbon feeds. It is particularly suitable for hydroprocessing heavy feedstocks of which at least 40 wt.%, preferably at least 60 wt.%, boils above 538°C (1000°F) and which comprise at least 0.1 wt.%, preferably at least 1 wt.%, of sulfur and at least 5 wt.% of Conradson carbon. The sulfur content of the feedstock may be above 2 wt.%. Its Conradson carbon content may be above 8 wt.%, preferably above 10 wt.%. The feedstock will contain contaminant metals, such as nickel and vanadium. Typically, these metals are present in an amount of at least 15 wtppm, calculated on the total of Ni and V, more particularly in an amount of at least 30 wtppm.

Suitable feedstocks include atmospheric residue, vacuum residue, residues blended with gas oils, vacuum gas oils, coker gas oils, crudes, shale oils, tar sand oils, solvent deasphalted oil, coal liquefied oil, etc. Typically they are atmospheric residue (AR), vacuum residue (VR), and mixtures thereof.

The hydrodemetallization catalyst used in the process according to the invention generally comprises a Group VIB metal component, preferably molybdenum, on a porous oxidic carrier. The catalyst may or may not also contain a Group VIII metal component, preferably nickel and/or cobalt, for reasons of economics and performance more preferably nickel. The Group VIB metal component is generally present in an amount of 1.5-20 wt.%, calculated as trioxide, more preferably 4-16 wt.%. If a Group VIII metal component is present in the hydrodemetallization catalyst, it is generally present in an amount of 0.3-6 wt.%, preferably 1-5 wt.%.

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The hydrodemetallization catalyst is based on a porous oxidic carrier. Preferably, the carrier comprises at least 50 wt.% of alumina, the balance being made up of oxides of one or more of silicon, titanium, or zirconium. Preferably, the carrier contains at least 75 wt.% of alumina, more preferably at least 95 wt.%.

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The hydrodemetallization catalyst may contain limited amounts of other ingredients known in the art as suitable for use in hydrodemetallization catalysts, including phosphorus, boron, alkaline metal components, and alkaline earth metal components.

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The demetallizationhydrodemetallization catalyst has a total pore volume which is generally between 0.2 and 1.4 ml/g, preferably 0.4-1.2 ml/g, more preferably 0.5-0.9 ml/g.

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The hydrodemetallization catalyst has a surface area of 50-250 m<sup>2</sup>/g, preferably 80-200 m<sup>2</sup>/g, more preferably 100-180 m<sup>2</sup>/g. If the surface area of the catalyst is too low, the catalytic activity will be insufficient. If the surface area of the catalyst is too high, the average pore diameter of the catalyst may be too low. The average pore diameter of the catalyst is defined in the context of the present specification as the pore diameter at which half of the pore volume is present in pores with a diameter above this value while the other half of the pore volume is present in pores with a diameter below this value. The hydrodemetallization catalyst used in the process according to the invention generally has an average pore diameter of 10-35 nm, preferably 15-30 nm, more preferably 20-30 nm, still more preferably 24-30 nm.

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It is preferred for the hydrodemetallization catalyst used in the process according to the invention to have less than 15%, more preferably less than 10%, of pore volume present in pores with a diameter below 100 Å.

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Hydrodemetallization catalysts suitable for use in the present invention are known in the art. They are, e.g., commercially available from Nippon Ketjen Co. Ltd under the designations KFR 10, KFR 20, KFR 22, and KG 5.

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The hydrodesulfurization catalyst to be used in the process according to the invention generally comprises a Group VIB metal component, preferably molybdenum, and a Group VIII metal component, preferably nickel and/or cobalt, more preferably nickel, on a porous oxidic carrier. The Group VIB metal component is generally present in an amount of 9-30 wt.%, calculated as trioxide, more preferably 10-27 wt.%. The Group VIII metal component is generally present in an amount of 2-12 wt.%, preferably 2-8 wt.%.

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The hydrodesulfurization catalyst is based on a porous oxidic carrier. Preferably, the carrier comprises at least 50 wt.% of alumina, the balance being made up of oxides of one or more of silicon, titanium, or zirconium. Preferably, the carrier contains at least 75 wt.% of alumina, more preferably at least 95 wt.%.

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The hydrodesulfurization catalyst may contain limited amounts of other ingredients known in the art as suitable for use in hydrodesulfurization catalysts, including phosphorus, boron, alkaline metal components, and alkaline earth metal components.

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The hydrodesulfurization catalyst has a total pore volume which is generally between 0.2 and 1.4 ml/g, preferably 0.4-1.2 ml/g, more preferably 0.5-0.9 ml/g. The hydrodesulfurization catalyst generally has a surface area of 50-400 m<sup>2</sup>/g, preferably 100-300 m<sup>2</sup>/g, more preferably 200-300 m<sup>2</sup>/g. If the surface area of the catalyst is too low, the catalytic activity will be insufficient. If the surface area of the catalyst is too high, the average pore diameter of the catalyst may be too low. The hydrodesulfurization catalyst used in the process according to the invention generally has an average pore diameter of 5-20 nm, preferably 7-15 nm, more preferably 7-12 nm.

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Hydrodesulfurization catalysts suitable for use in the present invention are known in the art. They are, e.g., commercially available from Nippon Ketjen Co. Ltd under the designations KFR 70, KFR 72, and KFR 70B.

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5 The hydrodesulfurization catalyst used in the first reactor, the hydrodesulfurization catalyst used in the second reactor and any hydrodesulfurization catalyst(s) used in any further reactor may be the same or different.

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10 The asphaltene removal catalyst used in the process according to the invention generally comprises a Group VIB metal component, preferably molybdenum, and a Group VIII metal component, preferably nickel and/or cobalt, more preferably nickel, on a porous oxidic carrier. The Group VIB metal component is generally present in an amount of 2-20 wt.%, calculated as  
15 trioxide, more preferably 4-16 wt.%. If the Group VIB metal content is too low, the activity of the catalyst will be impaired. If the Group VIB metal content is too high, the activity will not be improved further.

The Group VIII metal component is generally present in an amount of  
20 0.5-6 wt.%, preferably 1-5 wt.%. If the Group VIII metal content is too low, the activity of the catalyst will be impaired. If the Group VIII metal content is too high, the activity will not be improved further.

The asphaltene removal catalyst is based on a porous oxidic carrier.  
25 Preferably, the carrier comprises at least 50 wt.% of alumina, the balance being made up of oxides of one or more of silicon, titanium, or zirconium. Preferably, the carrier contains at least 75 wt.% of alumina, more preferably at least 95 wt.%. The asphaltene removal catalyst may contain limited amounts of other ingredients known in the art, including phosphorus, boron, alkaline metal  
30 components, and alkaline earth metal components.

The asphaltene removal catalyst has a total pore volume which generally is at least 0.4 ml/g, preferably at least 0.55 ml/g. The pore volume generally is at most 1.4 ml/g, preferably at most 1.2 ml/g, more preferably at most 0.9 ml/g. The asphaltene removal catalyst generally has a surface area of at least 50 m<sup>2</sup>/g and at most 200 m<sup>2</sup>/g, preferably 100-180 m<sup>2</sup>/g.

If the surface area of the catalyst is too low, the catalytic activity will be insufficient. If the surface area of the catalyst is too high, the average pore diameter of the catalyst may be too low. The asphaltene removal catalyst used in the process according to the invention generally has an average pore diameter of 10-35 nm, preferably 15-30 nm, more preferably 18-28 nm.

If the average pore diameter is too low, the decomposition of asphaltenes will be insufficient and excessive hydrogenation may take place to increase sludge formation. If the average pore diameter is too high, the asphaltene decomposition rate may also decrease, with inherent sludge formation.

It is preferred for the asphaltene removal catalyst used in the process according to the invention to have less than 15%, more preferably less than 10%, of pore volume present in pores with a diameter below 100 Å.

The asphaltene removal catalyst generally has 0.3 ml/g or less of pore volume in pores with a diameter of 100 nm or larger, preferably 0.2 ml/g or less. If the amount of pore volume present in this range is too high, the balance between the decomposition of the asphaltenes and the resins which act as their solvent is lost, and sludge is liable to be formed. Moreover, if the amount of pore volume present in this range is too high, the mechanical strength of the catalyst will decrease.

Asphaltene removal catalysts suitable for use in the present invention are known in the art. They are, e.g., commercially available from Nippon Ketjen Co. Ltd under the designations KFR 10, KFR 20, KFR 22, and KG 5.

5 The asphaltene removal catalyst used in the first reactor, the asphaltene removal catalyst used in the second reactor, and any asphaltene removal catalyst(s) used in any further reactor may be the same or different.

10 As can be seen from the above description, the asphaltene removal catalyst and the hydrodemetallization removal catalyst used in the process according to the invention are quite similar. This means that it is within the scope of the present invention for the demetallizationhydrodemetallization catalyst and the asphaltene removal catalyst to be used in the process according to the invention to be the same.

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15 The hydrodesulfurization catalyst used in the process according to the invention is always different from the hydrodemetallization catalyst and the asphaltene removal catalyst. More in particular, the hydrodesulfurization catalyst has a Group VIB metal content which is at least 2 wt.%, preferably at least 3 wt.%, higher than the Group VIB metal content of the hydrodemetallization catalyst and the Group VIB metal content of the asphaltene removal catalyst, calculated as trioxide.

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25 Additionally, the average pore diameter of the hydrodesulfurization catalyst is at least 1 nm, preferably at least 2 nm, more preferably at least 3 nm, below the average pore diameter of the demetallizationhydrodemetallization catalyst and the average pore diameter of the asphaltene removal catalyst.

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30 The catalyst particles may have the shapes and dimensions common to the art. Thus, the particles may be spherical, cylindrical, or polylobal and their

diameter may range from 0.5 to 10 mm. Particles with a diameter of 0.5-3 mm, preferably 0.7-2 mm, for example 1.2-1.5 mm, and a length of 1.5-10 mm, for example 2.5-4.5 mm, are preferred. Because they lead to a reduced pressure drop in ~~demetallization~~hydrodemetallization operations, polylobal particles may be preferred.

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If so desired, a small amount of the catalyst used in the top layer of one or more of the reactors may have a different particle shape and size for the purpose of regularising the flow of the feedstock passing through the reactor.

As is conventional in the art, the various types of catalysts can be present in a single bed in the unit, or in a number of beds one above the other containing the same type of catalyst.

The way in which the catalysts used in the process according to the invention are prepared is not critical. By way of example, a suitable preparation process is described below.

A typical production process for preparing a catalyst carrier comprising alumina is coprecipitation of sodium aluminate and ~~aluminum~~ sulfate. The resulting gel is dried, extruded, and calcined, to obtain an alumina-containing carrier. Optionally, other components such as silica may be added before, during, or after precipitation. By way of example, a process for preparing an alumina gel will be described below.

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First, a tank containing tap water or warm water is charged with an alkali solution of sodium aluminate, ~~aluminum~~ hydroxide or sodium hydroxide, etc., and an acidic ~~aluminum~~ solution of ~~aluminum~~ sulfate or ~~aluminum~~ nitrate, etc. is added for mixing. The hydrogen ion concentration (pH) of the mixed solution changes with the progress of the reaction. It is preferable that when the addition of the acidic ~~aluminum~~ solution is complete, the pH is 7 to 9, and that

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during mixing the temperature is 60 to 75°C. The mixture is then kept at that temperature for in general 0.5-1.5 hours, preferably for 40-80 minutes.

In a following stage, the gel is separated from the solution, and any commercially used washing treatment, for example a washing treatment using tap water or hot water, is carried out to remove impurities, mainly salts, from the gel. Then, the gel is shaped into particles in a manner known in the art, e.g., by way of extrusion, beading or pelletizing.

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Finally, the shaped particles are dried and calcined. The drying is generally carried out at a temperature between room temperature and up to 200°C, generally in the presence of air. The calcining is generally carried out at a temperature of 300 to 950°C, preferably 600 to 900°C, generally in the presence of air, for a period of 30 minutes to six hours. If so desired, the calcination may be carried out in the presence of steam to influence the crystal growth in the oxide.

By the above production process, it is possible to obtain a carrier having properties which will give a catalyst with the surface area, pore volume, and pore size distribution characteristics specified above. The surface area, pore volume, and pore size distribution characteristics can be adjusted in a manner known to the skilled person, for example by the addition during the mixing or shaping stage of an acid, such as nitric acid, acetic acid or formic acid, or other compounds as moulding auxiliary, or by regulating the water content of the gel by adding or removing water.

The Group VIB metal components and, where appropriate, Group VIII metal components or other components such as phosphorus, can be incorporated into the catalyst carrier in a conventional manner, e.g., by impregnation and/or by incorporation into the support material before it is shaped into particles. At this point in time it is considered preferred to first



prepare the carrier and incorporate the catalytic materials into the carrier after it has been dried and calcined.

The metal components can be incorporated into the catalyst composition in the form of suitable precursors, preferably by impregnating the catalyst with an acidic or basic impregnation solution comprising suitable metal precursors. For the Group VIB metals, ammonium heptamolybdate, ammonium dimolybdate, and ammonium tungstenate may be mentioned as suitable precursors. Other compounds, such as oxides, hydroxides, carbonates, nitrates, chlorides, and organic acid salts, may also be used.

For the Group VIII metals, suitable precursors include oxides, hydroxides, carbonates, nitrates, chlorides, and organic acid salts. Carbonates and nitrates are particularly suitable. The impregnation solution, if applied, may contain other compounds the use of which is known in the art, such as organic acids, e.g., citric acid, ammonia water, hydrogen peroxide water, gluconic acid, tartaric acid, malic acid or EDTA (ethylenediamine tetraacetic acid).

It will be clear to the skilled person that there is a wide range of variations on this process. Thus, it is possible to apply a plurality of impregnating stages, the impregnating solutions to be used containing one or more of the component precursors that are to be deposited, or a portion thereof. Instead of impregnating techniques, dipping processes, spraying processes, etc. can be used. In the case of multiple impregnation, dipping, etc., drying and/or calcining may be carried out in between.

After the metals have been incorporated into the catalyst composition, it is optionally dried, e.g., in air flow for about 0.5 to 16 hours at a temperature between room temperature and 200°C, and subsequently calcined, generally in air, for about 1 to 6 hours, preferably 1-3 hours, at 200-800°C, preferably 450-700°C. The drying is done to physically remove the deposited water. The

calcining is done to bring at least part, preferably all, of the metal component precursors to the oxide form.

It may be desirable to convert the catalysts, i.e., the Group VIB and optional Group VIII metal components present therein, into the sulfidic form prior to their use in the hydroprocessing of hydrocarbon feedstocks. This can be done in an otherwise conventional manner, e.g., by contacting the catalyst in the reactor at increasing temperature with hydrogen and a sulfur-containing feedstock, or with a mixture of hydrogen and hydrogen sulfide. *Ex situ* presulfiding is also possible.

In the present specification, the indications Group VIB metal and a Group VIII metal refer to the Periodic Table of Elements applied by Chemical Abstract Services (CAS system). The specific surface area is determined by nitrogen (N<sub>2</sub>) adsorption using the BET method.

The determination of the total pore volume and the pore size distribution is effected via mercury penetration at a contact angle of 140° with a surface tension of 480 dynes/cm, using, for example, a mercury porosimeter Autopore II (trade name) produced by Micrometrics.

Examples:

Three catalysts were selected for use in the present example.

The hydrodemetallization (HDM) catalyst contained 9 wt.% of molybdenum, calculated as oxide, and 2 wt.% of nickel, calculated as oxide, on an alumina carrier. The catalyst had an average pore diameter of 180 Å.

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The hydrodesulfurization (HDS) catalyst contained 12 wt.% of molybdenum, calculated as oxide, and 3 wt.% of nickel, calculated as oxide, on an alumina carrier. The catalyst had an average pore diameter of 120 Å.

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The asphaltene removal (HDAsp) catalyst contained 8.0 wt.% of molybdenum, calculated as oxide, and 2.2 wt.% of nickel, calculated as oxide, on an alumina carrier. The catalyst had an average pore diameter of 260 Å, a surface area of 130 m<sup>2</sup>/g, a total pore volume of 0.8 ml/g, and a pore volume in pores with a diameter of 1000 Å and larger of 0.25 ml/g.

The feedstock used in the present example was a South Sea atmospheric residue with the following properties:

sulfur	0.2 wt. %
nitrogen	3 000 wt. ppm
metals (nickel + vanadium)	70 wt. ppm
Conradson Carbon residue	7 wt. %
Asphaltenes <sup>1</sup>	2.5 wt. %
Density (15°C)	0.93 g/ml
Distillation properties ASTM-D 5307	
Initial boiling point	301°C
50 wt. %	563°C
70 wt. %	624°C

<sup>1</sup> matter insoluble in n-heptane

A small reactor system consisting of three reactors connected in series was packed with the selected catalysts. The packing of the reactors applied in Example 1 according to the invention and in the Comparative Example is given below:

	Example 1	Comparative Example
1 <sup>st</sup> reactor	HDM catalyst – 20 vol.%	HDM catalyst – 20 vol.%
	HDS catalyst – 55 vol.%	HDS catalyst – 80 vol.%
	HDAsp catalyst – 25 vol.%	
2 <sup>nd</sup> reactor	HDS catalyst – 75 vol.%	HDS catalyst – 100 vol.%
	HDAsp catalyst – 25 vol.%	
3 <sup>rd</sup> reactor	HDS catalyst – 95 vol.%	HDS catalyst – 100 vol.%
	HDAsp catalyst – 5 vol.%	

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After packing the reactor system with the respective catalysts, the catalysts were sulfided in a conventional manner by contacting them with a light gas oil (LGO) containing 2.5 wt.% of dimethyl disulfide (DMDS), and the feedstock described above was led to the reactor system at a pressure of 16.5 MPa, a liquid hourly space velocity (LHSV) of  $0.3 \text{ h}^{-1}$ , and a hydrogen to feed ratio ( $\text{H}_2/\text{oil}$  ratio) of 850 Nl/l. The reaction temperature was adjusted to achieve a Conradson Carbon residue content of 3.0 wt.% in the product oil, with the temperature in the second bed being higher than the temperature in the first bed in each reactor, while, if applicable, the temperature in the third bed was higher than the temperature in the second bed. The test was carried out for a period of 200 days.

In Example 1, where an asphaltene removal catalyst was present in the high-temperature bottom region of each of the three reactors, the process still operated well after 200 days, and could be continued after that date. By comparison, the process of the Comparative Example, where no asphaltene removal catalyst was present in the high-temperature bottom region of each of the three reactors, had to be discontinued on day 135, because the reactors were clogged with sludge.

The following table gives the temperatures of the various catalyst layers in Example 1 and the comparative Example.

	Example 1 (day 200)		Comparative Example (day 135)	
1 <sup>st</sup> reactor	HDM catalyst	390°C	HDM catalyst	390°C
	HDS catalyst	398°C	HDS catalyst	400°C
	HDAsp catalyst	405°C		
2 <sup>nd</sup> reactor	HDS catalyst	413°C	HDS catalyst	413°C
	HDAsp catalyst	422°C		
3 <sup>rd</sup> reactor	HDS catalyst	421°C	HDS catalyst	422°C
	HDAsp catalyst	423°C		

5 The processes of Example 1 and the Comparative Example were operated under such a regimen that the amount of Conradson carbon residue in the product was kept at 3.0 wt.%. This means that, as is conventional in the art of hydroprocessing, the reaction temperature is slowly increased to compensate for catalyst deactivation to keep the amount of Conradson Carbon residue in the  
10 product at the desired value.

Figure 4 shows the change of the average reaction temperature during the process at a constant Conradson Carbon content in the product for the process according to the invention and for the Comparative Example. It can be  
15 seen that for the process according to the invention of Example 1, the temperature increase stabilised to a value of less than 0.8°C per month. In contrast, for the Comparative Example, by the end of the run a temperature increase of 2°C per month was obtained.

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20 Apparently, even if the Conradson Carbon Content of the product is the same, the presence of an asphaltene removal catalyst in the high-temperature bottom end of the hydroprocessing reactors ensures that less sludge is formed,

which leads to less clogging of the unit and a longer and more stable operation. The presence of the asphaltene removal catalyst also appears to result in a more stable process, as can be seen from a lower increase in reaction temperature being necessary to keep the Conradson carbon content of the product at a value of 3.0 wt.%.  
5

Although not wishing to be bound by theory, the inventors believe that the presence of an asphaltene removal catalyst in the high-temperature lower end of the hydroprocessing reactors ensures that the decomposition of the asphaltenes and the resins which act as their solvents is well balanced, resulting in low sludge formation. On the other hand, it is believed that in the comparative example, where no asphaltene removal catalyst was present, the resins that act as solvent for the asphaltenes were hydrogenated. As a result, the asphaltenes became insoluble in the hydrocarbon feed, causing the formation of sludge. In turn, the presence of sludge caused deactivation of the catalyst due to coke being formed thereon.  
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## ABSTRACT

The invention pertains to a process for hydroprocessing a heavy hydrocarbon feed using at least two reactors in which a heavy hydrocarbon feed is subjected sequentially to the steps of

- hydroprocessing in a first hydroprocessing reactor, in which it is subjected sequentially to a hydrodemetallization step, a hydrodesulfurization step carried out at a temperature higher than that of said hydrodemetallization step, and an asphaltene removal step carried out at a temperature higher than that of said hydrodesulfurization step,
- hydroprocessing in a second hydroprocessing reactor, in which it is subjected sequentially to a hydrodesulfurization step and an asphaltene removal step, which latter is carried out at a temperature higher than that of said hydrodesulfurization step.

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